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NITRATE INTERFERENCE IN TOTAL KJELDAHL NITROGEN DETERMINATIONS AND ITS REMOVAL BY ANION EXCHANGE RESINS

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.

- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

The standard methods for analysis of water and waste samples are under continual review to assure that the most accurate results possible are obtained. If a chemical interference in an important analytical procedure is discovered it must be evaluated and if necessary a procedure modification made to circumvent the interference. This report investigates the interference of nitrate in the analysis for total Kjeldahl nitrogen and suggests a method for removing this interference.

Dwight G. Ballinger
Director
Environmental Monitoring and Support Laboratory

ABSTRACT

The interference of nitrate with the determination of total Kjeldahl nitrogen (TKN) was investigated. TKN losses of greater than 90% were observed in solutions containing a nitrate-nitrogen concentration ten times greater than the TKN level. The loss was found by infrared spectroscopy to be occurring due to nitrate and ammonia decomposition to nitrous oxide at the elevated TKN digestion temperatures. Prevention of the nitrate interference in TKN analyses was found to be possible only by removal of nitrate prior to TKN analysis. Several anion-exchange resins in the chloride form were found effective in this removal. Samples containing known TKN levels and high nitrate concentration when treated by these resins prior to TKN analysis gave nearly 100% TKN recovery on TKN analysis.

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Finally, the support of the U.S. Environmental Protection Agency in this grant is acknowledged. With this support Central State University faculty and students have had the invaluable opportunity of participating in important and relevant research work.

SECTION I

INTRODUCTION

Amounts of ammonia and organically bound nitrogen, called total Kjeldahl nitrogen (TKN), are determined by the Kjeldahl method,[1] a long-accepted standard method of analysis used for example, to evaluate the protein content of food. Recent work, however, has demonstrated that high nitrate concentrations result in low TKN analysis results. In some cases (nitrate levels 20-times greater than ammonia), greater than 90% of the Kjeldahl nitrogen present is lost in analysis. This plus the common natural occurrence of nitrate makes the study of its interference a significant one. The purpose of this study was to: (1) confirm this interference of nitrate in the Kjeldahl nitrogen determination, (2) understand the mechanism of the loss of nitrogen, and (3) find a simple, yet effective way to prevent the nitrate interference and enable accurate TKN determination of any sample.

SECTION II

SUMMARY

The work presented here demonstrates the interference of the nitrate ion in TKN determinations, a proposed mechanism of the interference, and one effective, simple way of eliminating the interference. The results show that nitrate-nitrogen significantly interferes with TKN determinations whenever the nitrate-nitrogen levels are ten-times or greater the Kjeldahl nitrogen levels. By collection of the gases released during a TKN determination and infrared analysis, the predominant product is found to be nitrous oxide. This gas unquestionably is formed through combination of ammonia and nitrate at the high temperatures (greater than 300°C) of the Kjeldahl digestion reaction. Subsequent loss through the digestion reaction causes lowered TKN results.

As the interference in the TKN determinations is a result of the presence of nitrate and the use of high temperatures during reflux, elimination of one or the other is necessary. Because the high temperature is necessary for decomposition of organic compounds, nitrate removal is the only feasible approach. The high solubility and low complexing ability of nitrate compounds led to the selection of ion exchange resins as a simple, effective way to remove the nitrate interference in TKN determinations. Several anion exchange resins in the chloride form were found effective in reducing nitrate-nitrogen levels of 25 ppm to essentially zero. Prior treatment of samples containing greater than 50 fold excess of interfering nitrate with these resins, followed by TKN analysis, resulted in quantitative recovery of the original TKN.

SECTION III

CONCLUSIONS

This work has demonstrated the following:

1. Accurate determination of TKN levels using the ammonia electrode requires use of standard ammonia solutions containing electrolytes to adjust the ionic strength to the level present in the sample.

2. Nitrate does indeed interfere and reduce the TKN in a sample when it is present in concentrations ten times or greater than the TKN level.

3. The loss of TKN when nitrate is present occurs by formation of nitrous oxide, due to the high temperature used in the Kjeldahl digestion.

4. The interference can only be prevented by removal of nitrate prior to TKN analysis. Anion-exchange resins in chloride form were found effective in this removal.

5. Nitrite seems also to interfere in TKN analysis when present in high concentration. This interference probably occurs due to the combining of ammonia and nitrite to release nitrogen gas. As nitrite is generally present in very low levels in natural water samples, this interference is probably not significant in most cases.

SECTION IV

RECOMMENDATIONS

As a result of this work the following need attention:

1. The need for ionic strength adjustment in standards when the ammonia electrode is used in TKN analysis should be noted.

2. The interference of nitrate in TKN analyses should be noted in the Methods for Chemical Analysis of Water and Waste manual, as well as the suggested (or another) procedure for elimination of this interference.

3. The evaluation of TKN analysis procedures different from the one used in this study needs to be made to determine the extent of nitrate interference. The effect of using block digestors with higher digestion temperatures needs to be investigated. The effect of a catalyst other than mercury (II) needs to be considered.

4. A re-evaluation of past TKN analyses should be made. Seawater, for example, can have nitrate levels as high as 0.7 ppm with TKN levels of 0.03 ppm, and interference would be anticipated. TKN determinations of run-off water in rural areas might be low due to high nitrate levels resulting from fertilizers. In some specific TKN applications, invalid low levels of Kjeldahl nitrogen could be reported due to high nitrate levels.

5. The interference of nitrite needs to be substantiated more thoroughly. The blocking of nitrite interference by anion-exchange resins should be confirmed.

6. Frequently, time-tested analytical procedures stifle efforts to develop new and better methods. Development of a faster, yet reliable way of releasing organic nitrogen than the Kjeldahl procedure needs to be considered. If such a procedure could be developed, nitrate interference might be avoided.

SECTION V

EXPERIMENTAL PROCEDURES

MEASUREMENTS

All electromotive potential readings in this report were taken using an Orion Model 801A digital pH/mv meter, an Orion Model 95-10 ammonia electrode, an Orion Model 90-02 double-junction reference electrode, and an Orion Model 94-17A chloride electrode. The infrared spectra were obtained using an IR-8 Beckman spectrophotometer and a Perkin-Elmer long path gas cell.

SOLUTIONS

All solutions in this work were prepared using distilled water deionized by a Corning Model LD-2a demineralizer.

Standard solutions of ammonia-nitrogen ranging from 100 ppm to 0.01 ppm were prepared using reagent grade ammonium chloride. To each solution were added a few drops of dilute hydrochloric acid to ensure against loss of ammonia. A second series of ammonia standards was prepared, containing ionic concentrations identical to those present in samples after distillation and digestion using TKN reagents. One liter of each of these standard solutions contained 26.7 g of K_2SO_4, 0.4 g of HgO dissolved in 5 ml of 1:5 sulfuric acid, and 40 ml of concentrated H_2SO_4--all of which were neutralized using 10 M NaOH before addition to the standard plus the required quantity of ammonium chloride.

The solutions needed for the Kjeldahl analysis were prepared as described in References 4 and 6. The 10 M NaOH (alkaline reagent 1) was prepared using reagent grade 50% NaOH solution purchased commercially. The alkaline reagent 2 (400 g NaOH, 300 g NaI and 2 g EDTA per liter) was likewise prepared using this 50% NaOH solution.

For most of this work, standard solutions of alanine were analyzed for TKN. A stock solution of alanine containing 50 ppm nitrogen was prepared using reagent grade alanine. This solution was prepared fresh every two weeks because it appeared to hydrolize somewhat within this interval.

Nitrate solutions containing 200 ppm nitrogen, 500 ppm nitrogen, and 100 ppm nitrogen were prepared using $NaNO_3$.

OPERATING PROCEDURE

The TKN determinations in this study were made by the modified procedure using an ammonia ion electrode (see References 4 and 5). In this procedure, 50.0 ml of sample are placed in a 100 ml round bottomed flask, and 10 ml of the sulfuric acid-mercury (II) sulfate-potassium sulfate solution (called TKN reagent) are added. The mixture is evaporated until SO_3 fumes are emitted, then is allowed to digest for 30 minutes. It is allowed to cool, and the residue is dissolved in distilled water, rinsed from the flask into a graduated cylinder, and diluted to 44 ml. An addition of 6 ml of 10 M NaOH neutralizes most of the sulfuric acid, resulting commonly in a pH between 3 and 5. The resulting solution is cooled in an ice bath to 25°C, a stirring bar added, stirring begun, and the ammonia electrode inserted. After adding 4 ml of alkaline reagent 2, a millivoltage measurement is made as soon as the reading stabilizes. Generally a 1-minute wait is sufficient although longer times are sometimes necessary for more dilute solutions.

Calibration curves of electrode potential versus the negative logarithm of parts per million ammonia-nitrogen were prepared periodically. These plots were linear and Nernstian over the concentration range of 0.1 ppm to 100 ppm. General operating procedure included measuring a standard solution both before and after each sequence of important measurements.

Apparatus for six simultaneous runs was available. For many important measurements an average of six determinations was made. In all cases determinations were made at least in triplicate.

SECTION VI

DATA

The results of this study will be reported in the following five sections:

1. The use of the ammonia electrode in TKN analyses,
2. Confirmation that the presence of nitrate causes low TKN results,
3. Analysis of the mechanism of nitrate interference in TKN analyses,
4. The use of anion-exchange resins to remove nitrate interferences in TKN analyses, and
5. Evidence for nitrite interference.

1. The use of the ammonia electrode in TKN analysis

The use of the ammonia electrode in TKN determinations is becoming increasingly widespread because it obviates distilling the ammonia from the sample and carrying out a titration.[6,7,8] In this approach the residue after Kjeldahl digestion is almost neutralized and diluted to 50 ml. Addition of akaline reagent 2 raises the solution pH to release the ammonia, simultaneously preventing precipitation of mercury or other metal hydroxides on the ammonia electrode membrane. Shortly after addition of alkaline reagent 2, the electrode millivoltage stabilizes and can be read.

Initially a series of standards was prepared using ammonium chloride ranging from 0.01 ppm to 100 ppm ammonia-nitrogen. A few drops of dilute HCl were added to each to ensure against ammonia loss. These standards, when made alkaline with 10 M NaOH, gave a linear plot of millivoltage versus log (ppm ammonia-nitrogen between 0.1 ppm and 100 ppm.) The plots were Nernstian commonly having a slope close to -59 millivolt/decade. However, a curve obtained from these standards consistently showed greater than 100% recovery of ammonia in TKN analyses of standard solutions. The cause of this error was the disparity between the standard solutions and the TKN solutions being analyzed. Although the ionic strength of the standard solutions is nearly zero, the ionic strength of the TKN solutions, containing H_2SO_4, K_2SO_4, and H_gSO_4, is greater than 2.5 M. This very large value could have a considerable influence on the polar ammonia molecule. To test this, the standards were prepared including identical to those of concentrations of H_gSO_4, K_2SO_4, and Na_2SO_4 (formed by neutralization of H_2SO_4) solutions resulting from TKN analysis. In Table 1 a comparison of the response of the ammonia electrode to standard solutions with and without the TKN reagent is shown.

TABLE 1. Comparison of the response of the ammonia electrode to standard solutions with and without TKN reagents for ionic strength adjustment

TKN Concentration	Millivoltage Standard Solution with TKN reagents	Standard Solution with TKN reagents
1.0 ppm	30.3 mvolt	21.9 mvolt
2.5	8.7	0.0
10	-25.9	-35.7

The above data demonstrate the presence of the TKN reagents causes a negative shift of the standard curve by 9.0 millivolts. The fact that the shift is constant for all readings implies an ionic strength effect rather than ammonia contamination. This result led to the use of standard solutions containing TKN reagents for all succeeding measurements to minimize experimental error.

2. Confirmation that the presence of nitrate causes low TKN results

The typical standard curve of the plot millivoltage versus the logarithm of the ppm of ammonia-nitrogen was linear and Nernstian over the concentration range 0.1 to 100 ppm ammonia-nitrogen. During this study, this standard curve shifted by ± 15 millivolts but always retained a slope very close to 59. To correct for these small shifts standard solutions containing TKN reagents were run at least twice daily and both before and after any readings deemed important.

Periodic measurements of the distilled, deionized water used in this study typically gave readings of 120 millivolts, implying less than 0.01 ppm ammonia-nitrogen. TKN analysis of 50 ml of this deionized water, 50 ml of a standard 2.0 ppm alanine solution, and 50 ml of 10.0 ppm NH_4Cl gave the results given in Table 2.

TABLE 2. TKN determinations of standard solutions

Sample	# of runs	Average Millivoltage (Deviation)	mg/l NH_3-N (Recovered)
Deionized water (blank)	5	75.0 (3.0)	0.2
2.0 ppm N (alanine)	3	-7.6 (.1)	2.5
10 ppm N (NH_4Cl)	3	-25.8 (1.2)	9.6

The rather large result for the blank apparently is the result of ammonia contamination of the reagents used and could not be lowered below the 0.2 ppm value given above. Difficulty in obtaining accuracy and precision with samples containing 1.0 ppm TKN or less, possibly due to the large blank, led to work with solutions containing 2.0 ppm TKN in many of the succeeding determinations.

The effect of large concentrations of nitrate-nitrogen on the results of TKN determinations of 50 ml of 2.0 ppm alanine are shown in Table 3.

TABLE 3. The effect of nitrate on TKN recovery

mg/l NO_3^--N	# of runs	Millivolts (Deviation)	mg/l TKN Recovered	% Recovery
0	3	-7.6 (.1)	2.5	100
5	3	13.8 (1.6)	2.3	92
20	3	72.4(20)	0.28	11
50	6	69.7 (7.2)	0.18	7

Great difficulty was experienced in obtaining good precision in TKN determinations made where high nitrate levels were present. The extent of ammonia loss seemed effected by distillation speed, temperature of the heating mantle, and, particularly, the amount of water left in each flask for digestion. Only by boiling all water from each solution and digesting the sulfuric acid-electrolyte solution remaining was satisfactory precision achieved. This aspect of the analysis will be discussed later in this report.

The data in Table 3 confirm other workers' observations (References 2 and 3) and illustrate the great magnitude of nitrate interference in TKN determinations.

3. Analysis of the mechanism of nitrate interference in TKN analyses

In order to determine a way of carrying out accurate TKN measurements without nitrate interference, a study of the mechanism of interference was undertaken. A literature search revealed that solid NH_4NO_3 decomposed slowly at 240°C [9] and rapidly at 290°C [10] into primarily nitrous oxide, N_2O, and water. Furthermore, chloride was thought to catalyze the reaction.[11] Measurement of the temperature during Kjeldahl digestion in several different determinations gave 312°C as an average reflux temperature. This temperature exceeds the literature values for decomposition of solid ammonium nitrate, and although a solution phase is present during the Kjeldahl digestion, this fact strongly supports decomposition as the mechanism of interference. To verify experimentally nitrous oxide loss during Kjeldahl nitrogen digestion, solutions were prepared containing various concentrations of ammonium and nitrate in concentrated sulfuric acid. Concentrated sulfuric acid was used as a solvent in these studies because its boiling point of about 315°C demonstrates that essentially concentrated sulfuric acid is the liquid phase in the Kjeldahl digestion.

The heating of two solutions of concentrated sulfuric acid, one containing ammonium nitrate to 10 ppm ammonia-nitrogen and the other 100 ppm NH_3-N (typical of the concentrations present during TKN digestion), gave the readings given in Table 4.

TABLE 4. Loss of TKN as a function of reflux temperature and time

Time of Sampling	Millivolts	
	10 mg/l NH_3-N	100 mg/l NH_3-N
Initial reading	+22.8	-3.2
180°C pot temperature	19.6	20.7
250°C " "	46.8	76.4
300°C " "	76.6	76.1
315°C " "	73.7	71.0
After one hour of reflux	78.2	72.2

These data indicate that solutions heated to over 300°C containing equal concentrations of ammonia and nitrate-nitrogen undergo significant decomposition and loss of Kjeldahl nitrogen. Furthermore, they demonstrate that the loss occurs quickly, before a temperature of 250°C, and that the percentage losses are very great, 95% for 100 ppm NH_3-N and 88% for 10 ppm NH_3-N. The surprising conclusion, nitrate reacts with ammonium in concentrated H_2SO_4 when both are present in concentrations as low as 10 mg/l, led to a determination of whether the Kjeldahl reagents inhibit this reaction. A solution of 40 ml concentrated H_2SO_4, 26.7 g K_2SO_4 and 1.0 g H_gSO_4 and 100 ppm NH_4NO_3 was heated, as above. Although it appeared that the decomposition required slightly higher temperatures, the same final effect was observed at about the same magnitude. With these data it appears the reason no decomposition is observed in TKN determinations when low levels of nitrate-nitrogen are present is the presence of greater quantities of water than those in the concentrated H_2SO_4 used in the above studies. As the proposed reaction shown causing TKN interference:

$$NH_4^+ + NO_3^- \longrightarrow N_2O + 2H_2O,$$

yields water as well as nitrous oxide, it would be expected that the presence of water in the reflux mixture would inhibit the decomposition. Thus the decomposition only becomes important when the nitrate-nitrogen levels are large relative to ammonia-nitrogen levels. If this is true, it would be expected that the nitrate interference would be of even greater significance where block digestors are used and higher, more water-free digestion temperatures achieved.

Confirmation of the presence of nitrous oxide in the gaseous effluent from the heating of ammonia nitrate in concentrated sulfuric acid was made by using infrared spectroscopy. The peaks at 1160 cm^{-1}, 1275 cm^{-1}, 2200 cm^{-1}, and 2560 cm^{-1} were used to confirm the presence of N_2O and semi-quantitatively evaluate its concentration. Infrared spectra revealed some nitrous oxide in the gaseous effluent of a solution of NH_4NO_3 in sulfuric acid containing 100 ppm ammonia-nitrogen heated to 230°C. Large quantities of nitrous oxide were formed when this solution was heated to 260°C and to 295°C. After heating to 315°C and refluxing for one hour, only traces of nitrous oxide were observed. Although the brown color of nitrogen dioxide was apparent from about 200°C upward, none was present in the infrared cell (perhaps because it was absorbed in the drying tube). Its presence presumably was due to decomposition of nitric acid formed during digestion.

In one final infrared study, loss of TKN from 50 ml of a solution containing 10 ppm ammonia-nitrogen and 100 ppm nitrate-nitrogen was found to occur within the first 5 minutes of digestion. Collection of the effluent gases during this period and subsequent infrared analysis showed the presence of nitrous oxide.

4. The use of anion-exchange resins to remove nitrate interferences in TKN analyses

From earlier work, the interference of nitrate in TKN determinations results from combination of nitrate and ammonium at elevated digestion temperatures with the subsequent loss of the Kjeldahl nitrogen as nitrous oxide. Prevention of the interference would only be possible by lowering the digestion temperature or prior removal of the nitrate. A few digestions carried out with only 90% of the sample water distilled and thus at a lower temperature resulted in incomplete recovery of the Kjeldahl nitrogen. This demonstrated that the water-free, high temperature is necessary to release all organic nitrogen in the Kjeldahl analysis. This conclusion mandated the physical removal of the nitrate prior to digestion as the only way to block the nitrate interference. The high solubility of all nitrate salts and the poor chelating ability of nitrate ruled out removal by precipitating or complexing. Anion exchange resins were studied for their potential in removing nitrate.

Dowex- 1 X 8 - 200 (100 to 200 mesh) anion exchange resin in the chloride form was used first in attempts to remove nitrate in the milligram -per-liter concentration range. A 5.00 g sample of the Dowex resin was washed several times with ammonia-free water. A chloride ion-selective electrode was inserted into 100 ml of stirred deionized water containing the resin. After a stable reading was achieved a few milliliters of 500 ppm nitrate-nitrogen solution were added. Instantly the millivoltage decreased, indicating the nitrate was being removed from solution replaced by the chloride from the resin. Within about ten seconds the millivoltage reading had stabilized again. To determine quantitatively the extent to which the resin removed nitrate, the previous experiment was repeated, adding 1.00 ml of 500 ppm nitrate-nitrogen to 100 ml of deionized water and 5.0 g of washed Dowex resin. The chloride-electrode responses after successive additions are given in Table 5.

TABLE 5. Addition of successive nitrate aliquots to distilled water and dowex -1 X 8 resin

Sample	Millivoltage Cl-electrode	mg/1 Cl^-	Increased in Cl^- in mg/1 Cl^-
Washed Dowex and 100 ml water	212.5	2.8	
Above + 5 mg/1 NO_3-N	176	15.5	12.7
+10ml/1 NO_3-N	160	31.6	16.1
+15ml/1 NO_3-N	152	44.7	13.1
+20mg/1 NO_3-N	146	57.6	12.9
+120mg/1 NO_3^- -N	121	182	124.4
+220mg/1 NO_3^- -N	110.5	295	113

For the first four additions up to 20 mg/1 NO_3^- -N, an average of 13.7 ppm Cl^- are released by each 5 ppm NO_3^- -N addition. By calculation 12.7 ppm Cl^- should be released for each ppm NO_3^- -N addition. This implies that nitrate is being quantitatively removed and replaced by chloride at these low concentrations. In increasing from 20 ppm to 120 ppm NO_3^- -N addition, only 124 ppm chloride is recovered, implying an only 50 percent exchange of resin chloride and solution nitrate. Treatment with a second portion of resin or treatment with a larger portion of resin would presumably remove all nitrate in these higher concentration.

With confirmation that nitrate could be removed by Dowex - 1 X 8 anion exchange resin, it was next necessary to confirm that the resin did not significantly increase the TKN blank. As this resin, like most anion exchange resins, is a quarternary ammonium salt, this concern was very real. A 5.0 g portion of Dowex resin was treated with 1.0 M NaOH to re-convert to the chloride form, and finally rinsed with several portions of distilled water. The rinsed resin was stirred with 50 ml of deionized water, the resin filtered from the water, and the filtrate analyzed by the usual Kjeldahl procedure. Analysis of three samples gave readings of 52.0 $\pm$ 0.5 millivolts. This corresponds to readings at the 0.5 ppm TKN level, an increase in TKN over the

deionized water blank level of 0.2 ppm. While some increase in TKN results from use of the resin, a run was made using the resin to remove nitrate prior to TKN determination. To a solution containing 2 ppm alanine-nitrogen and 50 ppm nitrate-nitrogen was added 5 g of rinsed Dowex resin. The solution was stirred, the resin filtered from the solution, and the filtrate analyzed in the usual manner. Analysis of three solutions gave an average reading of 12.8 ± 2.8 millivolts corresponding to that of 2.0 ppm TKN. Earlier determinations (see Table 3) without prior resin removal of the nitrate resulted in only 0.2 ppm TKN, or 7%, recovery in this analysis. An analysis using the same procedure with a solution containing 2 ppm alanine-nitrogen and 20 ppm NO_3^--N gave a millivoltage reading of 8.2 ± 1.7 for six runs, corresponding to readings for 3.2 ppm TKN. This increase, while difficult to explain, gives further evidence that all interfering nitrate had been removed.

Considering that the increase in TKN recovered might be due to contamination from the resin and being concerned with the larger blank (0.5 mg/l) resulting with use of the Dowex- 1 X 8 resin, other anion resins were investigated. Of the others studied, Permutit S-1 gave the best results. Blanks run on deionized water, after being stirred with this resin, filtered, and analyzed, gave an average for three determinations of 68.5 ± 2.2 millivolts. This compares very well with a blank reading run on deionized water, 75.0 millivolts. Thus, with Permutit S-1 very little TKN contamination results. Analysis of a solution containing 2 ppm alanine-nitrogen and 20 ppm nitrate-nitrogen after prior treatment with Permutit S-1 gave a reading of 17.2 ± 6.7 millivolts corresponding to readings of 2.2 mg/l TKN recovery. In a final determination analyses of a solution containing 5ppm alanine-nitrogen and 50 ppm nitrate-nitrogen gave results of 99.6 ± 6.1 millivolts without treatment and -.8 ± 1.4 millivolt with prior treatment. These values correspond to those of 0.1 and 4.5 ppm, implying a 90% recovery with treatment as compared to 2% recovery without. The data for these analyses are summarized in Table 6.

TABLE 6. The use of anion-exchange resins to remove nitrate for TKN analyses

mg/l TKN	mg/l NO_3-N	Anion Exchange Resin Treatment	# of runs	recovered TKN--mv	Recovered TKN mg/l	% recovery
2	50	None	6	69.7 ± 7.2	.2	7
0	0	Dowex-1 X 8	3	52.0 ± .5	.5	----
2	50	Dowex-1 X 8	3	12.8 ± 2.8	2.0	100
2	20	None	3	72 ±20	.3	11
2	20	Dowex-1 X 8	6	8.2 ± 1.7	3.2	160
0	0	Permutit S-1	3	68.5 ± 2.2	.3	----
2	20	Permutit S-1	3	17.2 ± 6.7	2.2	110
5	50	None	3	99.6 ± 6.1	0.1	2
5	50	Permutit S-1	3	-.8 ± 1.4	4.5	90

5. Evidence for nitrate interference

Although the nitrate concentration in natural water samples is commonly very low and well below TKN concentrations, its interference is possible in special TKN applications. The decomposition of ammonium nitrite into nitrogen and water occurs readily at even lower temperatures than ammonium nitrate decomposition, suggesting serious interference. Early in this project reduction of nitrate to nitrite was considered as a means to block the nitrate interference in TKN analysis. With this in mind the effect of nitrite in TKN determinations was investigated. Twelve runs were made determining the TKN concentration of a solution containing 2 mg/l of alanine and 50 mg/l of sodium nitrite. Although the precision was quite poor for these determinations, an average of only 20% recovery of TKN was found. The TKN analysis procedure had not been developed to a high precision at the time of these measurements, but interference of nitrite is clearly implied by the results.

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